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SUBJECT: A summary of research relevant to a WDNR proposed study of atmospheric mercury vertical flux

1) Memo background and purpose

In early June 2001 we in the Bureau of Air Management, Wisconsin Department of Natural Resources (WDNR, 2001) submitted a pre-proposal to the U.S. Environmental Protection Agency (US EPA). In this pre-proposal we are seeking funding support to design, set up and operate a field program to measure the near-surface gradient fluxes in atmospheric mercury (Hg) over several different types of land use / vegetative surfaces. The knowledge derived from this study will be used in the state's effort to run a computer model to more accurately simulate Hg transport, transformation and deposition processes.

To date almost all of the airborne Hg monitoring in Wisconsin has been either precipitation (wet) or mixed (combined wet and dry). The wet Hg measurements have been collected at several National Acid Deposition Program (NADP, 2001) sites, while the combined wet-dry Hg monitoring was conducted using IVL sensors (WDNR, 2000). Because there is a dearth of exclusively dry Hg measurements, the pre-proposal focuses on this type of flux monitoring, which is believed to make a substantial impact on ambient mercury levels.

The pre-proposal briefly describes a work plan, which includes a study design task. Since we have never conducted a flux measurement study of any air pollutant, much less one as complicated as Hg, we need to learn from those who have completed similar efforts, especially for Hg. Consequently, the purpose of this memo is to present my review of some published research on atmospheric Hg pollutant flux gradient studies that could be relevant to our proposed field design. This memo constitutes a contribution to the Study Design element in the proposed work plan. Other people will also be helping design this field program.

2) Pre-proposal overview

Our pre-proposal (WDNR, 2001) states the following summary design and intended results:

“The project will use a portable array of Tekran mercury monitors with speciation capability to measure the gradient of mercury compounds near the surface. The key to the study is the ability to test at various locations and at various times to more accurately calculate mercury mass flux under various conditions. These mass flux calculations will improve model estimates for the transport, transformation and deposition of mercury compounds.”

“The study design will identify various test locations through out the state. The test locations will include conifer forests, deciduous forests, croplands and other land use types that are significant from a mercury deposition perspective. The project will identify factors that influence surface mercury flux seasonally, such as temperature, foliage conditions and relative humidity. The sampling equipment will be moved from location to location in order to capture the various land use and meteorological conditions identified in the study design.”

3) Overview: Unique issues to address in measuring gradient fluxes in atmospheric Hg

Mercury is an air pollutant that has only within the past couple of decades received serious attention for its severe health consequences through the air-water-bioaccumulation pathway to fish and subsequently humans. Not being a criteria pollutant under the federal Clean Air Act makes Hg subject to less automatic regulatory review under provisions of that law. Most of the research conducted in atmospheric mercury so far has been done with the intention of developing some initial regulatory controls based upon the findings.

Furthermore, Hg is present in the atmosphere primarily as largely non-reactive elemental vapor [Hg^0] in fairly small concentrations (units: nanograms/ m^3 [ng/m^3]). However, the atmospheric Hg species that is of most serious impact to aquatic ecosystems and humans is reactive gaseous Hg (RGM, Hg^{2+}) and to a lesser extent particulate (Hg^p). The Hg^{2+} typically comprises only 3 – 6% of the already small total atmospheric Hg mass (e.g., Stratton and Lindberg, 2001) and have noticeably different characteristics (water soluble, faster removal rates) from Hg^0 . Additionally, Hg deposition is substantial due to both dry and wet (precipitation) processes, which require different monitoring approaches and equipment for different sub-species.

The precise monitoring of the vertical flux in any atmospheric pollutant is already a difficult task due to the need for optimally configuring fast response sensors to adequately quantify the pollutant's vertical gradient. However, EPRI (1998, p3-6) points out that for Hg fast response sensors are not yet available. So surrogate gas flux measurements (e.g., CO_2 , water vapor, etc..) need to be made along with multi-level Hg monitoring as well as vertical wind speeds and temperature profiles. Making this project even more complicated for Hg is that not only can it be re-emitted from previously-deposited fallout (Zhang, et. al., 2001) but that it has been shown to be significantly re-emitted from certain types of surfaces that are rich in Hg due to either anthropogenic activities (Lindberg, et. al., 1995) or natural (primarily geological) formations (e.g., Gustin, et. al., 1999). Adding to the complexity of Hg re-emissions, it has also been found that some of the Hg in soils (both anthropogenic and biogenic) is drawn up through the roots of trees into the trunks and emitted through the leaves (foliar surfaces) (Lindberg, Hanson, et. al., 1998).

Consequently, there is a considerable bi-directional air-surface exchange of Hg, indicating that a field of sensors measuring only fluxes in downward-moving Hg deposition could miss a significant component in the vertical Hg transport (Xu, et. al., 1999). Monitoring the net bi-directional flux in atmospheric (dry) Hg near the surface of several different land use types will be an even more challenging project than originally anticipated. This is especially true since we have never attempted such a complex research-grade monitoring effort in the past. We will definitely have to build upon the work of others who have conducted similar studies.

4) A review of previous Hg flux field studies

For reasons cited in Section 3, the volume of published research on atmospheric Hg flux monitoring is fairly modest when compared to many other topics in air pollution dynamics. Nevertheless, the amount of study on this subject that I actually reviewed is far from complete. To make this literature survey even more tentative is my novice understanding of the dynamics of atmospheric Hg transport and transformation processes, even when I moved rather cautiously through the material. Focusing my study on those portions of the research that I believe are relevant to the proposed field experiment has made this review a bit more manageable. Others contributing their assessments of these studies will also be very helpful in designing the field program.

a) Pre-1997 studies on Hg flux studies. Dr. Steven Lindberg has been involved in atmospheric Hg research for over 30 years, including almost every Hg flux measurement field study in the United States. Dr. Lindberg, who

is with the Environmental Studies Division of the Oak Ridge (TN) National Laboratory (ORNL ESD) has been a co-author on many papers that evaluate and interpret the design, execution and results of these Hg flux studies. The material in these papers is extremely complex and has taken awhile to read, digest, and synthesize the work described in these papers, especially for someone like me who is very unfamiliar with almost all monitoring operations. Nevertheless, I have attempted to identify those findings made in these Lindberg-contributed papers on some of the earlier (pre-1997) Hg flux work that might be relevant to us. These findings, which are presented in chronological order to allow the newer research to build upon the work done previously, are as follows:

- Refluxing mist chamber (RMC), which the WDNR Air Monitoring Section has one (never used yet). The description, initial use and results from an RMC is succinctly made by Stratton and Lindberg (1995). This project was not an actual Hg flux study but basically a test of a new monitoring design. This device was used to capture water-soluble reactive gaseous mercury (RGM, Hg^{2+}) for measurement. Monitoring at two locations during 1992 – 1994 found that the RMC found approximately $0.05 - 0.15 \text{ ng/m}^3 \text{ Hg}^{2+}$ (usually peaking in mid-day), which represented about 3 – 5 % of the total gaseous Hg (the remainder being primarily elemental (non-reactive) Hg (Hg^0)). They also found little correlation between Hg^{2+} and ozone, which they speculate argues against oxidation of the Hg^0 to Hg^{2+} . Most of this paper details the equipment, monitoring sites and field design, which might help us configure our flux measurement program. Of note is that this paper was published in 1995 and documents a study done 7 – 9 years ago. It is likely that there have been improvements made in the equipment, techniques and data validation methods since that time. We need to move up the learning the curve on how to optimally employ our RMC to help measure Hg^{2+} .
- Modified Bowen ratio-derived Hg^0 fluxes. Lindberg, *et. al.* (1995) introduces a micrometeorological gradient technique called the modified Bowen ratio (MBR) to quantify fluxes of elemental Hg (Hg^0) over Hg-contaminated soils (i.e., near a former weapons testing site) during the spring and fall of 1993. [*The WDNR has measured Hg in soil samples collected at the long-closed Badger Army Ammunitions manufacturing plant near Baraboo in 1998 (Olin, 2001). A thorough study of these data may give us a better focus on sampling the re-emission of Hg from the soil.*]

Lindberg (*et. al.*, 1995) points out that micrometeorological methods in measuring pollutant fluxes have the advantages over chamber / laboratory efforts of not disrupting the surface area being studied and the measurements provide a wider areal average (i.e., footprint) coverage of the flux. Reusable gold-plated quartz sand adsorbers were used to collect the gaseous Hg, of which typically 95-99% is comprised of Hg^0 . The Hg^0 was separated and quantified by a dual-amalgamation cold vapor atomic fluorescence spectrometry (CVAFS), which is described in succinct detail in the paper. Measurements of the Hg were taken at 1.65 m above the test soil area. Concurrent fast-response monitoring of temperature, wind speed, wind direction and water vapor at 0.25 m and 1.65 m above the test ground allowed for gradients in these variables. Since there are no fast-response Hg sensors the MBR used the derived meteorological gradients of water vapor to calculate a turbulent transfer coefficient. This calculation of trace gas water vapor was assumed to be representative of the turbulent transfer coefficient in Hg^{2+} and Hg^0 . The vertical turbulent fluxes for Hg^0 were estimated from these data and the measured vertical gradients in sensible heat and latent heat, which used eddy correlation techniques. Their measurements noted that wind direction and temperature can each have a strong influence on the amount of Hg^0 fluxes from contaminated soils. Lindberg also stresses that it is important to define the source of the signal reflected in the gradients and Hg^0 fluxes derived from them (i.e., “footprints”). This is especially true in natural settings where the re-emission of Hg is far from being uniform.

- Lindberg, Hanson, *et. al.* (1998) refined the field study that is described in Lindberg, *et. al.* (1995) – employing a tower-based micrometeorological gradient method (i.e., modified Bowen ratio [MBR]) for measuring both upward and downward (bi-directional) fluxes in Hg^0 over soils and several types of vegetation – an attempt to monitor many of the components in the full Hg biogeochemical cycle. They are careful to explain the justification for using the MBR method below a forest canopy, which would appear to be not appropriate. This field design might be more of what we are considering for our study, including the interest in bi-directional sampling over several varieties of vegetation. Some of the interesting findings in this paper include that the Hg^0 exchange at the surface is bi-directional but that is primarily characterized by emissions from plants and soil, where the temperature-driven volatilization of Hg^0 followed by diffusion to the surface are controlling factors to the emission rates. The relationship between soil temperature and Hg^0 is exponential and they assume that the Hg re-emissions are negligible at night. They speculate that the measured Hg re-emission gradients might be biased up to 40% low because of horizontal variability in the soil Hg. Dry deposition (foliar uptake) is less frequent, of lower magnitude and may be enhanced by surface wetness. They also establish that Hg emissions can occur in tree canopies through uptake in the tree trunks from soil pools. Re-emission or transpiration of Hg^0 from land is estimated to be significant, but requires further confirmation. They estimate that the 100 hectare test area emits a total annual Hg amount of approximately 1 – 10 kg / year.
- Lindberg and Stratton (1998) tackle the issue of measuring different speciated atmospheric Hg compounds. They provide a good overview of what is understood to be the chemical makeup and basic transformation processes involving atmospheric Hg. Lindberg and Stratton detail the results from several field studies that monitored the two general categories of total gaseous Hg (TGM: elemental $[\text{Hg}^0]$ and reactive gaseous [RGM, primarily Hg^{2+}]. Space constraints allowed only a brief description of the field studies, although they do confirm that the mist flux chamber (MFC, discussed by Stratton and Lindberg, 1995) is a viable method for quantifying RGM species, which they mention originates from combustion sources (perhaps power plants?), comprises only about 3% of the total gaseous Hg and is a highly surface-reactive species. They point out that speciation of airborne Hg is crucial to understanding how to better simulate its transportation, transformation and removal processes. For one, they note that Hg^0 is not water soluble but that Hg^{2+} is with the latter's water solubility strongly influences its removal processes and deposition rates from the atmosphere (more so in dry deposition, significantly less so during rain events). In general, the authors state that these findings support the hypothesis that Hg dry and wet deposition may be strongly influenced by the behavior of RGM. Their interpretation of the results, including some interesting graphical displays offers us some worthwhile guidance on how to analyze the Hg data collected in our field project, particularly in de-constructing the Hg gradient profiles under varying meteorological conditions.
- Rea, *et. al.* (2000) focused on the issue of Hg deposition to tree foliage, either by dry deposition or root / stomatal uptake from soil pools. In some locations fog can even be an important deposition mechanism. Net throughfall in Hg at the foliage interface (i.e., deposition minus leaching and washoff of dry deposition) represented a microscale study of bi-directional Hg fluxes at the leaf interface. The points in this study that might be most relevance to us would be derived estimates of Hg deposition velocities and leaching rates.
- Stratton, Lindberg and Perry (2001) update and refine their evaluation of the mist chamber (MC) method for measuring RGM species from their earlier research (Stratton and Lindberg, 1995). Their paper goes into detail on the MC design, detection limits, contamination, artifact formation, sampling duration, collection efficiency and data validation. Their discussion section poses substantive questions on the reasonableness, accuracy, bias, and artifacts contained in the RGM measurements made with an MC. This MC evaluation information, which should be considered relatively current, could help us optimize the design of any MC portion of our proposed field project, should we employ that equipment.

b) *The Nevada STORMS project.* In early September, 1997 the Nevada Study and Tests of the Release of Mercury from Soils (“STORMS”) was conducted at the Steamboat Springs geothermal area near Reno (Gustin, *et. al.*, 1999). Ten research institutions conducted a comprehensive field measurement project in which 4 different micrometeorological monitoring and 7 different flux chamber sites were set up to measure the Hg emitted from this geologically Hg-enriched soil area. A companion field study on soil-based Hg emissions (EPRI, 1998) was also conducted along side the STORMS project by the same research groups. There have been a fair number of research papers published on this project. A couple of these STORMS papers that appear to have some relevance to our proposal are as follows:

- Wallschlager, *et. al.* (1999) looked at the operations and results from 3 different parallel flux chamber tests. They note that the results agreed qualitatively among the 3 tests, but rather differently quantitatively among individual runs, especially during midday high emissions period and during nighttime deposition events. They conclude that both experimental differences and small-scale regional variability introduce large uncertainty in the estimates of Hg air-surface exchange gradients. They also found that rain events led to a strong increase in Hg emissions even when the covered soil remained dry – suggesting that the apparent chamber footprint is larger than the actual covered area. Their statistical analysis revealed strongest correlations between Hg fluxes and solar radiation and wind speed, weaker correlations with air and soil temperatures and wind direction. They briefly point out that the correlations between flux chamber-derived data and data derived from micrometeorological methods (e.g., modified Bower ratio [MBR]) were much worse – with the latter measuring Hg fluxes approximately 4 times those of the chamber techniques. The authors attribute much of this discrepancy to problems that are specific to the test area. This paper notes the difficulties and shortcomings in Hg flux measurement studies and how they might be mitigated in future experiments. Such information would be useful in helping us avoid similar mistakes in designing, conducting and analyzing our field work.
- Edwards, *et. al.*, (2001) expands upon and updates the STORMS work done by Wallschlager, *et. al.* (1999) studying the data collected at the 4 micrometeorological sites and 7 flux chamber monitors. Their findings include that the micrometeorological flux was enhanced up to 5-fold during rain events, day-time fluxes were greater than night-time fluxes by a factor of 6 and that temporal variations in climate factors affect the variability in total gaseous mercury flux (TGM). The STORMS surface test area was 200 meters x 200 meters and originally thought to be relatively homogeneous in its Hg content. However, the wide range in results among the various micrometeorological and chamber experiments on such a small area stressed 1) how extremely careful a field test must be set up to avoid any noise, bias or artifacts in the measured signal and 2) substrate sampling is important in quantifying the degree of spatial variability in surface soil Hg concentrations, emissions and fluxes. The findings contained in this STORMS paper would be very helpful in fine-tuning how to design our field experiment so as to minimize any errors in the sampling, data reduction, validation and analysis. Perhaps more importantly, this paper outlines the difference in techniques, operations, data collection, analysis and results for these two general method types in measuring Hg fluxes (i.e., flux chamber and micrometeorological). We can learn a lot from this paper in deciding if we should try to measure Hg fluxes with either one method or try both.
- EPRI (1998), although slightly older than both Wallschlager, *et.al.* (1999) and Edwards, *et.al.*, (2001), this report is valuable in describing the STORMS project because it is able to go into much more detail than either of these previously-discussed papers. The amount of description in all 7 chamber methods and 4 micrometeorological techniques offers a solid foundation on which we can more explicitly design for either technique or both in our Hg flux field study. Many of the numerous points of this report’s relevancy to our proposed work are contained in this memo’s Section 5.

c) *Michigan Tahquamenon River watershed Hg air / surface exchange study*. Zhang, *et. al.* (2001) discuss their 1998 field project to investigate vertical fluxes in Hg over 5 different site types of background soils in the Tahquamenon watershed of Michigan's Upper Peninsula. Their findings included that even measured re-emitted Hg from previously-deposited Hg over these soils were, as expected, rather small, especially in shaded areas. This type of study area is important to us in that we would likely consider setting up a field experiment in a similar type of soil-forest-vegetation ecosystem. Indeed, the Tahquamenon watershed could be very much like a northern Wisconsin area. Further making this monitoring a project a good template for ours is that it employed a Tekran automated Hg analyzer and flux chamber. We own one flux chamber and co-own two Tekran analyzers that presumably would be available for monitoring. However the study only looked at Hg immediately near the surface and did not consider bi-directional fluxes in Hg, which is what we probably want to do.

Among their findings from this study: solar radiation and irrigation were found to most influential to Hg air/surface exchange over shaded background soils, variation in mean Hg flux at different sites is strongly influenced by the variation in soil temperature, which can be greatly influenced by solar radiation, and that Hg dry deposition was observed even at a heavily-shaded forest site over wet soils.

d) *The Florida Everglades Dry-Deposition Study (FEDDS)*. The FEDDS, which is still an on-going study, was designed to test the viability of new and existing monitoring methods to estimate speciated Hg dry deposition over the Florida Everglades. Marsik, *et. al.* (2000) describe some of the preliminary results from the 1999 FEDDS field study. Of all the projects mentioned in this memo, the FEDDS monitoring study might possibly contain the most elements that could be appropriate for use in our proposed study, save for no wet-deposition monitoring being done. The FEDDS included direct total Hg dry deposition measurements using a water-based, surrogate-surface technique developed by the University of Michigan Air Quality Lab, as well as flux chamber (FC) and a micrometeorological measurement measurements whose data were plugged into an inferential dry-deposition model.

All 3 categories of atmospheric Hg (elemental [Hg^0], reactive gaseous [Hg^{2+}] and particulate [Hg^p]) were separately measured (a first according to the authors) for the same field study. Dynamic flux chambers and the modified Bowen Ratio (MBR) were employed to measure the bi-directional fluxes in Hg^0 . The MBR technique used measurements of trace gases (CO_2) and the eddy correlation method to obtain inferred fluxes in Hg from the ecosystem. The FC method directly measured Hg concentration changes over a known area, from which dry deposition and emission rates could be directly computer. The FC-derived data would help identify spatial flux patterns and for testing Hg flux mechanisms. Of additional importance to our proposal is it would be logical to assume that the design and implementation of the FEDDS field project was configured based upon the lessons learned in other Hg flux studies mentioned previously in this memo. Namely, the relatively new FEDDS should be expected to have the fewest errors in its design and implementation of any of the Hg flux experiments discussed in this memo. Another point of support to our study is their use of the Tekran 2537A Hg analyzers, which is the same model that we co-own (with Michigan and Minnesota) and would be employing in our study.

5) A synthesis of relevant research findings (identified in Section 4) as they may influence our proposed field project design

It is apparent from the research findings presented in Section 4 that our intentionally-brief pre-proposal will need to be revised substantially more than previously envisioned in order to make it worthwhile for any potential funding. Specific questions and issues that need to be addressed in refining our proposed scope of work are as follows:

- a) *How do we more precisely pose the questions and issues that we want to resolve through this proposed field study?* Our pre-proposal's problem statement focused primarily on measuring Hg dry deposition, which would complement the data base of Hg wet deposition samples collected through the National Acid Deposition Project (NADP, 2001) and the combined Hg wet-dry monitoring conducted by the WDNr (2000). Our pre-proposal also would more specifically measure the Hg dry flux employing a vertical array of ambient monitors (presumably something like the Tekran 2537A analyzers, of which the WDNr already co-owns two such instruments). The pre-proposal would also include wet Hg deposition sampling to obtain a full estimate of the net Hg loading to the study surface area(s). Assuming these Hg wet and net dry deposition estimates, measured over land, are representative of what would be witnessed over water, then it might be possible to quantify the net Hg loading to lakes, ponds, rivers and other water bodies, from which the continuing Hg pathway goes through a series of biochemical processes in the waters and sediments that cause the Hg to react with organic matter to form the highly toxic methyl mercury (MeHg). The MeHg is taken up by plants and animals – bioaccumulating in the aquatic food chain, climaxing with ingestion of MeHg-laden fish by humans.
- b) *What type of Hg flux measurement study do we want to conduct?* The Nevada STORMS project, which included 7 different flux chamber (FC) studies and 4 different micrometeorological (MM) studies. Edwards, *et. al.*, (2001) and EPRI (1998) both indicate that there are relative strengths and weaknesses with each type of flux monitoring. EPRI states that flux chambers are ideal for assessing physicochemical processes which drive mercury flux. This helps to quantify the magnitude of the influence of individual factors on flux because the correlation with environmental parameters was stronger than when employing MM techniques. On the other hand, the MM methods derive a Hg flux that represents the full (unconstrained) system which allows an assessment of the actual magnitude and fluxes occurring from an area.

Of note is that FEDDS effort (Marsik, *et. al.*, 2000) has followed the STORMS Project design by also conducting a combined FC / MM measurement study. I can only speculate that the FEDDS researchers saw evidence in the STORMS project that there were advantages to conducting both FC and MM investigations of bi-directional fluxes in various forms of atmospheric Hg. I think that we should also strongly consider doing the same type of FC / MM field project, assuming that funding would support a wider effort. One way to make the cost of such a combined investigation more reasonable would be to reallocate the proposed capital (i.e., equipment) cost expenditures to obtain instrumentation that would allow us to do both FC and MM monitoring over the same surface area. This FC / MM monitoring could be conducted concurrently over several different types of surfaces with each area being studied in sequential order.

- c) *Mercury monitoring equipment that the WDNr already owns for an FC study.* Substantial cost savings on our proposed Hg flux study could be accomplished by including those monitoring resources that the WDNr already owns. The FC method largely would require equipment to separate out the water-soluble reactive gaseous Hg (RGM – largely Hg^{2+} which is important for conversion to the highly toxic methyl mercury [MeHg]) from the non-water soluble elemental Hg (Hg^0). This would be done with the mist flux chamber (MFC), which the WDNr has one – but has never used. These samples could be analyzed either through an on-site Tekran 2537A analyzers (the WDNr co-owns 2 such instruments) or in a lab. The Hg^0 would be quantified by running ambient air samples through a Tekran 2537A analyzer of which we have had a little (4 days) operational experience in measuring Hg^0 . In order to measure fluxes in both Hg^0 and / or Hg^{2+} and use one Tekran 2537A analyzer – we would need a Tekran Automated Dual Sampling (TADS) System, which allows alternative monitoring at two different locations (e.g., heights). EPRI (1998, p. 3-8) describes a method for accomplishing this feat of monitoring the flux with only half the information available at each height (and neither height concurrently) and being assured of having accuracy and completeness within 5% of having a sampler running continuously at both heights. We do co-own at least one of these TADS.

Consequently, use of the two separately-located Tekran 2537A / TADS pairs would allow us to run an FC project with Hg^{2+} / Hg^0 flux gradients being measured at two separate locations (if we have 2 TADS). Employing one Tekran 2537A / TADS pair with the mist flux chamber (MFC) could conceivably measure the Hg^{2+} flux, while the other Tekran 2537A / TADS pair could focus monitoring the Hg^0 flux. However, even with access to this equipment, we still have a long way to go in learning how to configure, set up, test and operate them to obtain acceptable data. Furthermore, in our pre-proposal we are seeking US EPA funding to purchase and run 5 additional Tekran monitors with speciation capabilities in this study.

- d) *Prospects of employing a micrometeorological method (MM) to measure Hg flux.* An MM Hg flux study would appear to require a Tekran 2537A / TADS (for measuring Hg at least two different heights), as well as monitoring the following parameters with response sensors at these same heights: a surrogate trace gas such as water vapor or carbon dioxide (CO_2), horizontal wind speeds and directions, vertical wind speeds and temperature (EPRI, 1998, p. 3-7). These data would be used along with eddy correlation calculations and the modified Bowen Ratio (MBR, see memo Section 4a or Lindberg, *et.al.*, 1995 for more details on this technique) to calculate the turbulent transfer coefficients (and subsequently vertical flux) for Hg^0 and Hg^{2+} .

It appears that the instrumentation necessary to do a Hg MM flux field project, save for the Tekrans, are not included in the pre-proposal's capital equipment request. If a Hg MM study does gain more credibility in the next proposal draft, it will be necessary to include a careful evaluation of the instrumentation required for such a study, as well as estimating the costs to obtain, set up and employ them. Perhaps some of the allocation for five (5) Hg speciation monitors in the current pre-proposal could be reassigned to help cover the cost of any MM-related equipment.

- e) *Prospects of measuring particulate Hg (Hg^p).* Monitoring for Hg^p is not explicitly included in the pre-proposal. Furthermore, it is not known as to the amount of contribution that Hg^p makes to the total Hg or whether it is significant to the atmospheric Hg chemistry. Nevertheless, the possibility of monitoring this Hg specie, along with a cost estimate for the equipment necessary to do so should at least be investigated. Particulate Hg data would help give us a more complete understanding of the total atmospheric Hg loading in the study area(s). Marsik, *et. al.*, (2000) note that they measured Hg^p using 47mm glass fiber filters in teflon open-faced filter packs, with the samples analyzed in a class 100 room using methods described by Keeler, *et.al.*, (1995).
- f) *Mercury wet deposition monitoring.* Almost all Hg concentrations collected so far in Wisconsin has been monitored as result of either wet deposition (NADP, 2001) or combined wet-dry deposition (WDNR, 2000). A major issue in Hg deposition is determining under which circumstances (weather, Hg species, surface types) how much Hg is deposited due to either wet or dry deposition, respectively. Lindberg, *et.al.* (1998) showed that concentrations of the water-soluble reactive gaseous mercury (primarily Hg^{2+}) decreased sharply during rain events. However, Edwards, *et.al.*, (2001) measured a 5-fold increase in the water-non-soluble Hg^0 after rain events. Lindberg, *et.al.* (1998) hypothesized that Hg dry and wet deposition may be strongly influenced by the behavior of RGM. Consequently, it would be very beneficial to maintain that part of the pre-proposal that calls for wet deposition monitoring to be completed along side the dry deposition flux measurements.
- g) *Where to conduct the flux study?* The principle concern of Hg is its deposition onto water bodies, from where it is biologically transformed into the highly toxic methyl mercury (MeHg) and bioaccumulates as it works its way up the aquatic food chain to, in some cases, fish consumed by humans. However, the Hg monitoring sites in Wisconsin have been only near, not directly on lakes or rivers. However, several studies

have shown that there is a substantial amount of Hg that emanates from surface soils that are rich in Hg, either from anthropogenic activities (e.g., Lindberg, *et. al.*, 1995) or geological formations (e.g., Edwards, *et. al.*, 2001). Zhang, *et. al.*, (2001) has even measured re-emitted Hg from previously-deposited Hg over background soils in a river forest ecosystem in Michigan's upper peninsula. This last study noted these concentrations were, as expected, rather small, especially in shaded areas. The authors speculate that these values are probably due to historically low loading of Hg deposition in this region and / or Hg desorption and leaching in the region's sandy soils. The Zhang research is fairly relevant to our flux proposal because we might likely set up some monitoring in a similar water-forest ecosystem. If that turns out to be case, the Zhang findings suggest that it could be questionable as to whether monitoring the upward component in Hg flux from the surface in largely Wisconsin forest and or lake areas would be worthwhile. This very important issue needs to be further explored during the next stage in designing the field study.

It is not known if there are any areas in Wisconsin whose geological formations have resulted in Hg-rich surface soils such as those found in Nevada and studied as part of the STORMS project (Gustin, *et.al.*, 1999). On the other hand, it may be possible that there are some surface areas in the State that have Hg concentrations noticeably above background levels due to anthropogenic activities. This speculation is based upon some initial Hg concentrations collected from surface soils on the Badger Army Ammunitions Plant (Olin, 2001). This seemingly-Hg contaminated area might constitute one candidate study location (of several) for our Hg flux investigation.

6) Conclusions and recommendations

This memo has been an attempt to reflect my review, distillation and occasional synthesis of the some (certainly not all) published research on field projects designed to quantify the fluxes in various species of atmospheric Hg during the past 10 years or so. My focus during the literature review was on those portions that might perhaps be appropriate in helping us design and implement our own proposed Hg gradient flux study. Being neither a chemist, monitoring technician nor familiar with atmospheric Hg processes, this review has proven to be extremely challenging (to put it mildly). Attempting to have my evaluations relevant to our proposal required a lot of careful reading and re-reading, honing in on the basics for each paper – its purpose, description and findings that could be applicable to our proposed work.

The actual discussion of my review, contained in sections 4 and 5 of this memo does offer some understanding into research that we may build upon in conducting our field study. Based upon what I consider a preliminary evaluation of this work, we have a lot of strong precedent that will be useful to us.

We obviously have a long way to go from reading the findings, conclusions and ideas presented in these research papers to the actual design of a field project that would be successful. If anything comes through consistently in each of the papers referenced in this memo – it is that the reasonably accurate measurement of atmospheric Hg fluxes is far more complex than any monitoring project ever attempted in the WDNR Bureau of Air Management. Consequently, we need to take extra special caution so that making this proposal a reality results in a significant contribution to the understanding of Hg dynamics.

Monitoring technicians and chemists need to review these studies discussed here too since they are much better versed in the real world of field measurements. They can certainly visualize better than me on what is being described in this research. We can also build upon the Hg monitoring that has already been conducted in Wisconsin – by the WDNR, those running the Hg portion of National Acid Deposition Project (NADP, 2001), the US EPA's Lake Michigan Mass Balance Study (LMMB), etc...

We can also move up the learning curve on atmospheric Hg flux studies by contacting some of the researchers listed in this memo. They may be able to provide guidance on specific questions or concerns that we may have on our field design, set up, implementation and data interpretation. Indeed, several of these researchers (e.g., Professor. Jerry Keeler, Dr. Steve Lindberg) have already had contact with DNR staff on some Hg monitoring studies in Wisconsin and elsewhere.

All in all, this memo represents a good initial step, but only one early step on our path towards better understanding atmospheric Hg processes in Wisconsin. But there is very much that still needs to be accomplished.

7) References

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